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(54) **Durable compositions and use of same.**

(57) Provided is an acid catalyzed curable composition comprising a polyfunctional hydroxy group containing material, a triazinetriss-carbamate and an acid cure catalyst. The curable composition can furthermore contain an aminoresin crosslinking agent. These curable compositions have desirable lower cure temperatures, lower formaldehyde emissions during cure, and produce films and objects which have superior environmental etch resistance than conventional aminoresin crosslinked compositions. Further described is the use of these curable compositions to form solid articles or to produce adhesives or coatings.

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The present invention refers to curable compositions and use of the same.

Aminoresin based coatings are well known in the art and have been used for nearly half a century in diverse applications including general industrial coatings, automotive coatings, coil coatings, powder coatings, baking enamels, and wood finishes. Among the major drawbacks of aminoresin based coatings are formaldehyde emissions during cure and poor environmental etch resistance of the cured coatings.

Alkyl and aryl 1,3,5-triazine-2,4,6-tris-carbamates and coatings prepared therefrom have been described in EP-A-0 541 966 and in U.S. Pat. Nos. 5,084,541 and 4,939,213. Coatings prepared by using 1,3,5-triazine-2,4,6-tris-carbamate crosslinkers have been found to possess generally satisfactory properties, particularly regarding etch resistance. These systems, however, are tin-catalyzed systems of high cost and generally require relatively high bake temperatures to cure. They also yellow to some extent in part due to the high bake temperatures required for cure.

It is therefore the object of the present invention to provide curable compositions which avoid the above mentioned drawbacks. This object is solved by the curable compositions according to independent claims 1 and 14, the method of coating a substrate according to claim 17, the film or object according to independent claim 21 and the use of the curable compositions according to independent claim 22. Further advantageous features, aspects and details of the invention are evident from the dependent claims, the description and the examples. The claims are to be understood as a first non-limiting approach to define the invention in general terms.

The present invention relates to curable compositions containing polyfunctional hydroxy group containing materials and a triazinetriscarbamate, preferably 1,3,5-triazine-2,4,6-tris-carbamates. The present invention also relates to aminoresin containing curable compositions which additionally contain a triazinetriscarbamate, preferably a 1,3,5-triazine-2,4,6-tris-carbamate as a co-crosslinking agent. Both compositions contain an acid cure catalyst.

The present invention provides coatings which have the advantages of aminoresin based systems such as low cost and low cure temperatures, and the advantages of triazinetriscarbamate based systems such as good environmental etch resistance and absence of formaldehyde emissions during cure, without the drawbacks of either system.

We have discovered, surprisingly, that when a carbamate co-crosslinking agent is added to conventional aminoresin based curable compositions, the following major deficiencies of such compositions are overcome:

(1) the high formaldehyde emissions normally encountered in aminoresin derived curable compositions during cure are reduced to lower levels; and

(2) coatings produced from curable compositions containing a carbamate co-crosslinking agent have superior environmental acid etch resistance when compared with conventional aminoresin coatings.

Accordingly, described herein is a curable composition which comprises, as an additive to the commonly used aminoresin curable compositions, a triazinetriscarbamate, preferably 1,3,5-triazine-2,4,6-tris-carbamate co-crosslinking agent.

During the formulation of the present invention, it was additionally surprisingly discovered that curable compositions containing polyfunctional hydroxy group containing materials and triazinetriscarbamates could be effectively catalyzed, and cure temperatures lowered, via acid catalysts common to aminoresin crosslinked systems. In its broadest aspects, therefore, the present invention is a curable composition comprising:

(1) a polyfunctional hydroxy group containing material;

(2) a triazinetriscarbamate; and

(3) an acid cure catalyst.

In preferred aspects, the present invention is a curable composition, comprising:

(a) a polyfunctional hydroxy group containing material;

(b) an aminoresin crosslinking agent;

(c) a triazine triscarbamate co-crosslinking agent; and

(d) an acid cure catalyst.

The preferred triazinetriscarbamates are 1,3,5-triazine-2,4,6-tris-carbamates.

These compositions have low cure temperatures and low formaldehyde emissions during cure, and further produce films and objects which have superior environmental etch resistance than conventional aminoresin derived coatings.

The curable compositions of the present invention have utility in coatings, such as general industrial coatings, automotive coatings, coil coatings, powder coatings, baked enamels, and wood finishes. They are also usable as molding and adhesive compositions.

The present invention is also an improved method of coating comprising contacting a substrate with the curable compositions of the invention and thereafter heat curing.

Polyfunctional Hydroxy Group Containing Materials

The polyfunctional hydroxy group containing materials usable in the curable compositions of the invention are those conventionally used in aminoresin coatings and are capable of reacting with aminoresin crosslinking agents and/or with carbamate crosslinking agents.

Suitable polyfunctional hydroxy group containing materials include, for example, polyols, hydroxyfunctional acrylic resins containing pendant or terminal hydroxy functionalities, hydroxyfunctional polyester resins containing pendant or terminal hydroxy functionalities, hydroxyfunctional polyurethane prepolymers, products derived from condensation of epoxy resins with an amine, and a mixture thereof. Acrylic and polyester resins are preferred.

An example of a suitable polyfunctional acrylic resin available commercially from S. C. Johnson & Sons, Inc., is JONCRYL® 500 acrylic resin, comprising a copolymer of styrene (50%), hydroxypropyl methacrylate (20%) and butyl acrylate (30%) having the following properties:

Solids Content (%)		80
Hydroxyl Number (based on solids)		140
Equivalent Weight (based on solids)		400
Viscosity	(mPa.s)	4000
	(centipoise)	4000
Molecular Weight, Number Average		1,300
Molecular Weight, Weight Average		2,210
Polydispersity		1.7

A similar resin is also available from Rohm & Haas under the trademark AT-400.

Other examples of suitable polyfunctional hydroxy group containing materials include commercially available polyester resins such as CYPLEX® 1531, a polyester of phthalic acid, adipic acid, ethanediol, and trimethylolpropane, a product of Cytec Industries, West Paterson, New Jersey; CARGIL POLYESTER 5776 available from Cargill Corporation; TONE® polylactone resins available from Union Carbide Corporation; K-FLEX® XM-2302 and XM-2306, a product of King Industries, Norwalk, Connecticut; and CHEMPOL® 11-1369, a product of Cook Composites and Polymers, Port Washington, Wisconsin.

Aminoresin Crosslinking Agents

The aminoresin crosslinking agents usable in the curable compositions of the invention are partially or fully methylolated, substantially fully etherified amino compounds such as melamine, glycoluril, guanamine, and urea. They may be monomeric or oligomeric, the oligomeric forms arising from the self condensation of the monomeric forms under acidic conditions, and particularly under acidic conditions at super ambient temperatures. The aminoresin crosslinking agents of the invention are further characterized by having at least 2, and preferably more than 2 crosslinkingly reactive groups such as alkoxymethyl groups per crosslinker molecule.

The aminoresin crosslinking agents usable in the curable compositions of the invention are exemplified further hereinbelow.

Melamine-based aminoresin crosslinking agents are well known in the art and have been used extensively as effective crosslinkers in coatings. The alkoxymethylmelamine functionality can be a maximum of six in a crosslinkingly effective range of 2 to 6 alkoxymethyl groups per each melamine molecule. In addition to monomers, alkoxymethyl melamines can contain dimers, trimers, tetramers, and higher oligomers, each given combination of comonomers and oligomers being preferred for a given application. For example, the lower viscosity monomer-rich compositions are preferred for solvent-based high solids coatings.

An example of the substantially fully etherified, substantially fully methylolated, substantially monomeric melamines usable in this invention is CYMEL® 303 melamine crosslinking agent, a product of Cytec

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Industries, West Paterson, New Jersey, having the following physical and chemical properties:

Non-Volatiles (% by weight)*	98
Color, Maximum (Gardner 1963)	1
Viscosity (Gardner-Holt, at 25 °C)	X-Z
Free Formaldehyde, maximum (wt %)	0.5
Degree of Polymerization	1.75

* Foil Method (45 °C/45 min).

An example of a partially methylolated, substantially fully etherified partially oligomeric melamine-formaldehyde resin is CYMEL® 323 melamine crosslinking agent, a product of Cytec Industries, West Paterson, New Jersey, having the following properties:

Principal Reactive Group		NHCH ₂ OCH ₃
Solvent		Isobutanol
Degree of Polymerization*		2.2
Non-Volatiles (% by weight **)		80 ± 2
Viscosity (Gardner-Holt, at 25 °C)		Y-Z ₃
Viscosity	(Pa.s, approximate)	3.0-7.1
	(Poise, approximate)	30-71

* Degree of Polymerization: Average number of triazine units per molecule.

** Foil method (45 °C/45 min).

An example of the substantially fully etherified, substantially fully methylolated, substantially monomeric mixed alkyl melamines is CYMEL® 1168 melamine crosslinking agent, a product of Cytec Industries, West Paterson, New Jersey. The alkyl group in CYMEL® 1168 consists essentially of a mixture of methyl and isobutyl groups. It has the following properties:

Non-Volatiles (% by weight)*	98
Color, Maximum (Gardner 1963)	1
Viscosity (Gardner-Holt, at 25 °C)	X-Z
Free Formaldehyde, maximum (wt %)	0.5
Equivalent Weight	150-230

* Foil Method (45 °C/45 min).

An example of a substantially methylolated, partially etherified, substantially oligomeric melamine is CYMEL® 370 crosslinking agent, a product of Cytec Industries, West Paterson, New Jersey. It has the following properties:

Non-Volatiles (% by weight)*	88 ± 2
Solvent	Isobutanol
Color, Maximum (Gardner 1963)	1
Viscosity (Gardner-Holt, at 25 °C)	Z ₂ - Z ₄
Equivalent Weight	225-325

* Foil Method (45 °C/45 min).

The preferred glycoluril crosslinkers of this invention are N-alkoxymethyl substituted glycolurils wherein at least two of the alkyl groups in the alkoxymethyls are selected from a group consisting of methoxymethyl, ethoxymethyl, propoxymethyl, butoxymethyl, pentoxymethyl, hexoxymethyl, heptoxymethyl, octox-

ymethyl nonoxymethyl, decoxymethyl and mixtures thereof, and the remaining alkyl groups are selected from hydrogen, alkyl, hydroxymethyl, and glycoluril group-containing oligomeric moieties.

While it is preferable to have 4 alkoxymethyl groups per each glycoluril crosslinking agent, under ordinary circumstances it may not be necessary to obtain the pure tetrasubstituted monomeric crosslinker N,N',N'',N'''-tetraalkoxymethylglycolurils, so that resinous materials are normally usable.

The monomeric tetraalkoxyglycolurils themselves are not considered to be resinous materials since they are, as individual entities, non-polymeric compounds. They are considered, however, to be potential resin-forming compounds when subjected to heat, and particularly when subjected to heat under acidic conditions. As a result of the described resin-forming ability, the substantially monomeric glycoluril crosslinkers of this invention may contain some higher oligomeric components such as dimers, trimers, and tetramers. The presence of modest amounts of these oligomeric forms is permissible and indeed beneficial in cases where a high melting solid crosslinker is desirable as it is the case in powder coatings.

An example of glycoluril crosslinker of this invention is POWDERLINK® 1174 Powder Crosslinking Agent, a product of Cytec Industries, West Paterson, New Jersey, and has the following properties:

Non-Volatiles, minimum (% by weight)	98
Appearance	White to pale yellow granulated flakes
Melting Point (°C)	90-110 °C
Average Molecular Weight	350
Equivalent Weight	90-125

Another example of a glycoluril crosslinker of this invention is CYMEL® 1170 fully butylated glycoluril crosslinker, a product of Cytec Industries, West Paterson, New Jersey, having the following properties:

Non-Volatiles, minimum (% by weight)	95
Appearance	Clear liquid
Color, Maximum (Gardner, 1963)	3
Viscosity (Gardner-Holt, 25 °C)	X-Z ₂
Molecular Weight, Average	550
Equivalent Weight	150-230
Methylol Content	Very low

As in melamines, the partially or fully methylolated or etherified alkyl and aryl guanamine aminoresins, both in their monomeric and oligomeric forms, are usable as crosslinking agents in this invention, with the selection depending on the particular application or the properties desired in the product.

Benzoguanamine, cyclohexylcarboguanamine and acetoguanamine aminoresins are also preferred as crosslinkers in this invention.

An example of a benzoguanamine-based crosslinking agent is CYMEL® 1123 resin, a product of Cytec Industries, West Paterson, New Jersey, wherein the alkyl in the alkoxymethyls is a mixture of methyl and ethyl groups.

An example of a urea crosslinker usable in this invention is BEETLE® 80 butylated urea formaldehyde resin, a product of Cytec Industries, West Paterson, New Jersey, having the following properties:

Non-Volatiles (% by weight)*	96 ± 2
Solvent Tolerance (ASTM D1198-55)	> 500
Color, Maximum (Gardner 1963)	1
Viscosity (Gardner-Holt, at 25 °C)	X-Z ₂

* Foil Method (45 °C/45 min).

It is evident from the discussions above, that a person skilled in the art, in selecting the most suitable crosslinker for a particular application, may choose a mixture thereof which imparts a balance of properties desired for that particular application.

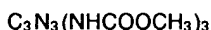
TriazineTris-Carbamates

The triazinetriscarbamates preferably the 1,3,5-triazine-2,4,6-tris-carbamate usable in the curable compositions of the invention have the following formula:



wherein R in each NHCOOR group is independently selected from the group consisting of an alkyl of 1 to 20 carbon atoms, an aryl of 6 to 20 carbon atoms, an aralkyl of 7 to 20 carbon atoms, and a mixture thereof.

The preferred carbamate crosslinking or co-crosslinking agents are carbamates wherein the R group is an alkyl group of 1 to 8 carbon atoms. Particularly preferred are 2,4,6-tris-(methoxycarbonylamino)-1,3,5-triazine represented by the formula:



and 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine represented by the formula:



and a mixture thereof.

The carbamate co-crosslinking agents may be prepared by procedures described EP-A-0 541 966 and in U.S. Pat. Nos. 5,084,541 and 4,939,213, the contents of which are incorporated herein by reference.

Cure Catalysts

As set forth herein, the curable composition optionally also includes a cure catalyst. As is recognized in U.S. Patent Nos. 5,084,541 and 4,939,213, a tin catalyst is typically required when a curable composition contains a 1,3,5-triazine-tris-carbamate derivative as the sole crosslinking agent. Uncatalyzed or acid catalyzed curable compositions containing 1,3,5-triazine-2,4,6-tris-carbamate derivatives remain hitherto unreported.

It is the discovery of this invention to provide acid catalyzed curable compositions capable of simultaneous cure by the aminoresin crosslinkers and the 1,3,5-triazine-tris-carbamate co-crosslinkers present therein.

The cure catalysts usable in the curable compositions of the invention include sulfonic acids, aryl and alkyl acid phosphates and pyrophosphates, carboxylic acids, sulfonimides, mineral acids, and mixtures thereof. Of the above acids, sulfonic acids are preferred. Examples of sulfonic acids include benzenesulfonic acid, paratoluenesulfonic acid, dodecylbenzenesulfonic acid, naphthalenesulfonic acid, dinonylnaphthalenedisulfonic acid, and a mixture thereof. Examples of the dialkyl acid pyrophosphates include phenyl, methyl, ethyl, diphenyl, dimethyl and diethyl acid phosphates and pyrophosphates. Examples of carboxylic acids include benzoic acid, propionic acid, butyric acid, formic acid, oxalic acid, trifluoroacetic acid, and the like. Examples of the sulfonimides include dibenzenesulfonimide, di-para-toluenesulfonimide, methyl-paratoluenesulfonimide, dimethylsulfonimide, and the like. Examples of the mineral acids include nitric acid, sulfuric acid, phosphoric acid, polyphosphoric acid, and the like.

Ratio and Proportions of the Ingredients

In the practice of the invention, a crosslinkingly effective amount of an aminoresin crosslinking agent and a triazinetriscarbamate, preferably a 1,3,5-triazine-2,4,6-tris-carbamate co-crosslinking agent is used. It is desirable to crosslink at least one half of the hydroxy functionalities present in the polyfunctional hydroxy group containing material to obtain coatings of good physical and resistance properties. It is preferred, however, that the mole ratio of the hydroxy groups to the sum of the crosslinkingly effective functionalities present in the aminoresin crosslinking agent and the triazinetriscarbamate co-crosslinking agent is in the range of from 0.8:1 to 1.2:1.

The weight ratio of the aminoresin crosslinking agent to the carbamate co-crosslinking agent usable in the curable composition of the invention are typically in the range of from 99:1 to 0.2:1. The weight ratio of the polyfunctional hydroxy group containing material to the sum of the aminoresin crosslinking agent and the carbamate co-crosslinking agent is in the range of from 99:1 to 0.5:1. The weight percent of the acid

cure catalyst to the sum of the polyfunctional hydroxy group containing material, the aminoresin crosslinking agent, and the carbamate co-crosslinking agent is in the range of from 0.01 weight percent to 3 weight percent.

5 Optional Ingredients

The optional ingredients present in the curable composition of the invention vary depending on the intended use of the cured article or film.

Suitable optional ingredients include fillers, ultraviolet light stabilizers, pigments, flow control agent, 10 plasticizers, mold release agents, and corrosion inhibitors.

The composition of the invention may contain as an optional ingredient a liquid medium. Such a medium may be used to aid the uniform application and transport of the curable composition. Any or all of the ingredients of the composition may be contacted with the liquid medium. Moreover, the liquid medium may permit formation of a dispersion, emulsion, invert emulsion, or solution of the curable composition 15 ingredients. Particularly preferred is a liquid medium which is a solvent for the curable composition ingredients (a), (b), (c), and (d). Suitable solvents are selected from alcohols, ketones, ethers, esters, water, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons and mixtures thereof.

Methods of Coating

20 Another aspect of this invention is a method of coating a substrate by contacting said substrate with a curable composition comprising:

- (1) a polyfunctional hydroxy group containing material,
- (2) a triazine tris-carbamate, preferably a 1,3,5-triazine-2,4,6-tris-carbamate, and
- 25 (3) an acid cure catalyst;

and thereafter heat curing said curable composition to produce a crosslinked film or object.

Another method of this invention is an improved method of coating a substrate by contacting said substrate with a curable composition comprising:

- (1) a polyfunctional hydroxy group containing material;
- 30 (2) an aminoresin crosslinking agent;
- (3) a Triazine tris-carbamate co-crosslinking agent, preferably selected from the group consisting of:
 - (i) a 1,3,5-triazine tris-carbamate of the formula $C_3N_3(NHCOOR)_3$, wherein R in each $NHCOOR$ group is independently selected from the group consisting of an alkyl of 1 to 20 carbon atoms, an aryl of 6 to 20 carbon atoms, an aralkyl of 7 to 20 carbon atoms, and a mixture thereof,
 - 35 (ii) an oligomer of (i), and
 - (iii) a mixture of (i) and (ii); and
- (4) an acid cure catalyst;

and thereafter heat curing said curable composition to produce a crosslinked film or object.

In the practice of the methods of the invention, the curable compositions of the invention containing the 40 triazine tris-carbamate, preferably the 1,3,5-triazine-2,4,6-tris-carbamate, co-crosslinkers are typically formulated as a liquid paint and applied onto a substrate by a method such as padding, brushing, rollercoating, curtain coating, flowcoating, electrostatic spraying, electrocoating or dipping. The coated substrate thereafter is heat cured at a temperature typically in the range of from 90°C to about 140°C to effect crosslinking and producing cured films or objects.

45 For powder coating applications, solid ingredients and higher temperatures in the range of 175°C to 190°C are typically used. "Powder coating" is an art recognized coating process and is defined herein as a method of electrostatic powder spraying wherein a finely divided solid coating material is electrostatically attracted to a surface of an article.

Alternatively, the powder coating composition may be contacted with the substrate by immersing the 50 substrate in fluidized bed of powder. The article covered with the powder is heated to at least the fusion temperature of the coating composition forcing it to flow out and form a coating which is cured by further application of heat.

For coil coating applications, temperatures typically in the range of 180°C to 360°C are used to cure.

55 Crosslinked Articles and Coatings Formed by the Compositions of this Invention

The curable compositions of this invention containing the carbamate co-crosslinkers of the invention can be heat cured (typically 90°C to 140°C) to produce crosslinked molded articles, adhesives and coatings.

Because of the polyfunctional nature of the reactants, the resulting product in this case is a crosslinked article in the form of a film such as adhesives or coatings or in the form of an article such as molded products and objects.

The heat-cured compositions of this invention may be employed as coatings for wire, appliances, automotive parts, furniture, pipes, machinery, and the like. Suitable surfaces include glass, plastics, wood and metals such as steel, and aluminum.

The heat-cured compositions may also be used to form solid articles such as cases, enclosures, and structural members.

The following Examples illustrate various embodiments of the invention.

10

EXAMPLE 1

Preparation of Acrylic COPOLYMER A

The polyfunctional hydroxy group containing material ACRYLIC COPOLYMER A was prepared as follows:

COPOLYMER A was prepared by admixing COPOLYMER B (70.2g), COPOLYMER C(63.5g), and normal butyl acetate (13.3g).

Preparation of COPOLYMER B

A first stream of a solution containing tertiary butyl peroctoate (28.94g), tertiary amyl perbenzoate (5.11g), and meta-xylene (11.35g) and a second stream of a solution containing methyl methacrylate (231.9g), styrene (62.6g), normal butyl acrylate (27.5g), and hydroxyethyl acrylate (178.8g) were simultaneously introduced, over a period of 5 hours, into a flask containing meta-xylene (305g) at 138 °C to 140 °C. After heating at 140 °C for an additional 3 hours, a portion of the volatiles (about 85g) was removed to give COPOLYMER B having the following properties:

30

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40

% Solids	71.2
% Hydroxide	3.58
Molecular Weight:	
Number Average	4,000
Weight Average	7,900
Polydispersity	1.97
Glass Transition (Tg)	
By DMA (°C)	57 ± 2
By DSC (°C)	38 ± 1

Preparation of COPOLYMER C

The procedure for preparation of COPOLYMER B was repeated with the following changes:

First Stream: 38.56g TRIGONOX 29-B75 Initiator 38.56
12.86g Meta-Xylene

Second Stream: 232.2g Methyl Methacrylate
101.4g Normal Butyl Acrylate
165.8g Hydroxyethyl Methacrylate
202.7g Meta-Xylene in the Flask.

The product formed was COPOLYMER C having the following properties:

55

% Solids	78.7
% Hydroxide	3.19
Molecular Weight:	
Number Average	3,900
Weight Average	8,600
Polydispersity	2.20
Glass Transition (Tg)	
By DMA (°C)	40 ± 1
By DSC (°C)	22 ± 1

EXAMPLE 2

Three coatings derived from a composition containing the hydroxyfunctional acrylic resin COPOLYMER A of EXAMPLE 1 and 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine were heat-cured with:

- (1) para-toluenesulfonic acid (COATING A)
- (2) dimethyl tin dilaurate (COATING B)
- (3) no catalyst (COATING C)

The coatings were formulated, applied onto base-coated panels and cured as follows:

	COATING		
	A	B	C
Acrylic COPOLYMER A of Example 1 (g):	73.3	73.3	73.3
2,4,6-tris-(Butoxycarbonylamino)-			
1,3,5-triazine (g):	26.7	26.7	26.7
Catalyst:			
(1) para-Toluenesulfonic acid (g):	0.5	---	---
(2) Dimethyl Tin Dilaurate (g):	---	0.5	---
(3) No Catalyst:	---	---	0.0

Substrate, White Base-Coated Panels: ED-11 CRS*

Cure Schedule (Table 1): 125°C/30 min.

(Table 2): 135°C/30 min.

* ED-11 primed cold rolled steel (CRS) is a product of Advanced Coating Technologies, Inc., Hillsdale, MI.

The cured coatings A, B, and C were thereafter analyzed for performance. The results are summarized in Table 1 for 125°C/30 min. cure schedule and in Table 2 for 135°C/30 min. cure schedule coatings.

TABLE 1

SOLVENT RESISTANCE* OF 2,4,6-TRIS-(BUTOXYCARBONYLAMINO)-1,3,5-TRIAZINE CONTAINING COMPOSITIONS IN ACID CATALYZED, TIN CATALYZED, AND UNCATALYZED COATINGS CURED AT 125 ° C/30 MINUTES SCHEDULES				
		COATING A	COATING B	COATING C
Thickness	(mils) (mm)	1.8 0.046	1.8 0.046	1.9 0.048
Hardness	KHN ₂₅ Pencil	12.4 H-2H	12.5 H-2H	12.4 H-2H
Methyl Ethyl Ketone				
Rubs	to Mar to Remove	200 + 200 +	200 200 +	100 200 +
Yellow Index,				
Original		-3.9	-3.9	-4.0
After 1st 30 min Overbake		-3.9	-3.9	-4.0
After 2nd 30 min. Overbake		-3.8	-3.8	-3.9

* Solvent Resistance is measured by Methyl Ethyl Ketone (MEK) Double Rubs "to mar" or "to remove" the coating. Highly crosslinked coatings require 200 + (i.e. more than 200) MEK Rubs to mar.

TABLE 2

SOLVENT RESISTANCE* OF 2,4,6-TRIS-(BUTOXYCARBONYLAMINO)-1,3,5-TRIAZINE CONTAINING COMPOSITIONS IN ACID CATALYZED, TIN CATALYZED, AND UNCATALYZED COATINGS CURED AT 135 ° C/30 MINUTES SCHEDULES				
		COATING A	COATING B	COATING C
Thickness	(mils) (mm)	1.8 0.046	1.9 0.048	1.8 0.046
Hardness	KHN ₂₅ Pencil	14.4 H-2H	13.2 H-2H	13.4 H-2H
Methyl Ethyl Ketone				
Rubs	to Mar to Remove	200 + 200 +	150 200 +	100 200 +
Yellow Index,				
Original		-2.3	-2.4	-2.4
After 1st 30 min Overbake		-2.0	-2.0	-2.0
After 2nd 30 min. Overbake		-1.7	-1.9	-1.8

* Solvent Resistance is measured by Methyl Ethyl Ketone (MEK) Double Rubs "to mar" or "to remove" the coating. Highly crosslinked coatings require 200 + (i.e. more than 200) MEK Rubs to mar.

EXAMPLE 3

A coating prepared using the curable composition of the invention, COATING D, was compared with a conventional aminoresin coating, COATING E.

5 COATING D and COATING E were formulated, applied onto base-coated panels and cured as follows:

	COATING D	COATING E
Acrylic COPOLYMER A of EXAMPLE 1 (g):	73.3	73.3
CYMEL® 303 Aminoresin Crosslinker:	13.4	26.7
2,4,6-tris-(Butoxycarbonylamino)-1,3,5-triazine (g):	13.4	0.0
para-Toluenesulfonic Acid (g):	0.4	0.4
Substrate, White Base-Coated Panels:	ED-11CRS	ED-11CRS
Cure Schedule (Table 3):	125 ° C/30min	125 ° C/30min

The cured coatings were thereafter analyzed for performance. The results are summarized in Table 3.

TABLE 3

PHYSICAL AND RESISTANCE PROPERTIES OF COATING D AND COATING E			
		COATING D	COATING E
Thickness	(mils)	1.8	1.8
	(mm)	0.046	0.046
Hardness	KHN ₂₅	13.1	13.3
	Pencil	H-2H	H-2H
Methyl Ethyl Ketone			
Rubs, to Mar		200 +	200 +
Adhesion, Top Coat to Base Coat		5	5
Yellow Index,			
Original		-4.5	-4.7
After 1st 30 min Overbake		-4.4	-4.7
After 2nd 30 min Overbake		-4.3	-4.6
Xenon Weathering, 1585 Hours,			
Yellow Index		2.5	3.0
Gloss 20 ° /60 °		69/83	67/84

EXAMPLE 4

The experiment in EXAMPLE 3 was repeated with the exception that instead of CYMEL® 303 resin, high imino group containing CYMEL® 323 resin was used and instead of the paratoluenesulfonic acid catalyst, somewhat weaker dimethyl acid pyrophosphate cure catalyst was used. Thus, COATING F contained both an aminoresin crosslinker and a tris-carbamate co-crosslinker, whereas COATING G contained only the aminoresin crosslinker for comparison.

The cured coatings were thereafter analyzed for performance. The results are summarized in Table 4.

TABLE 4

PHYSICAL AND RESISTANCE PROPERTIES OF COATING F AND COATING G			
		COATING F	COATING G
Thickness	(mils) (mm)	1.7 0.043	1.6 0.041
Hardness	KHN ₂₅ Pencil	12.5 H-2H	13.9 H-2H
Methyl Ethyl Ketone			
Rubs	to Mar to Remove	200 + 200 +	200 + 200 +
Adhesion, Top Coat to Base Coat		5	3
Yellow Index,			
Original		-4.2	-4.4
After 1st 30 min Overbake		-4.2	-4.4
After 2nd 30 min Overbake		-4.1	-4.2
Xenon Weathering, 1585 Hours,			
Yellow Index		-2.8	-3.6
Gloss 20°/60°		75/87	66/83

EXAMPLE 5

The environmental etch resistance of COATINGS D, E, F, and G was determined as follows:
2 drops of an acid was added to the surface of a coating at room temperature and thereafter heated to 50 °C for 20 minutes. Then, the appearance of the coating was examined visually and the changes noted.

COATINGS D, E, F, and G were tested for environmental etch resistance as described above using:

- (a) aqueous sulfuric acid (0.1 Normal); or
(b) aqueous phosphoric acid (0.1 Normal).

The results using sulfuric acid are summarized in Table 5 and those using phosphoric acid are summarized in Table 6.

TABLE 5

ENVIRONMENTAL ETCH RESISTANCE OF COATINGS D, E, F, AND G USING 0.1 NORMAL SULFURIC ACID	
COATING	TEST RESULTS
D	Contact area swelled
E	Contact area etched down to base coat
F	Contact area swelled
G	Contact area swelled and severely cracked

TABLE 6

ENVIRONMENTAL ETCH RESISTANCE OF COATINGS D, E, F, AND G USING 0.1 NORMAL PHOSPHORIC ACID		
COATING	TEST RESULTS	
D	Contact area swelled	
E	Contact area was partially etched away	
F	Contact area swelled	
G	Contact area swelled and severely cracked	

EXAMPLE 6

A coating using the curable composition of the invention, COATING H, was compared with a conventional aminoresin, COATING I.

COATING H and COATING I were formulated, applied onto base-coated panels, and cured. The formulations comprise the following:

	COATING H	COATING I
TA 39-14 Acrylic resin* (g)	72	65
CYMEL® 1170 Crosslinker (g)	14	35
2,4,6-tris-(Butoxycarbonylamino)-1,3,5-triazine (g)	14	0
para-Toluenesulfonic Acid (g)	0.6	0.6
Substrate, White Base-Coated Panels	ED-11 CRS	ED-11 CRS
Cure Schedule	125 °C/30 min	125 °C/30 min

* TA 39-14 Acrylic Resin is a product of Dock Resins Corp., Linden, N.J. having an equivalent weight of 450.

The cured coating were thereafter analyzed for performance. The results are summarized in TABLE 7.

TABLE 7

		COATING H	COATING I
Thickness	(mils)	1.88	1.65
	(mm)	0.048	0.042
Hardness	KHN ₂₅	5.7	4.2
	Pencil	H-2H	F-H
Methyl Ethyl Ketone			
Rubs to Mar		200 +	200 +
Adhesion, Top Coat to Base Coat		5	3
Yellow Index,			
Original		-1.8	-1.9
	After 1st 30 min Overbake	-1.1	-1.1
	After 2nd 30 min Overbak	-0.9	-1.0
Gloss 20°/60°, Original		86/93	85/93

EXAMPLE 7

The procedure of EXAMPLE 5 was repeated using COATING H and COATING I. The results are summarized in TABLE 8 (sulfuric acid) and TABLE 9 (phosphoric acid).

TABLE 8

ENVIRONMENTAL ETCH RESISTANCE OF COATING H AND COATING I USING 0.1 NORMAL SULFURIC ACID	
COATING	TEST RESULTS
H	Contact area swelled in rings
I	Contact area severely swollen and and slightly cracked

TABLE 9

ENVIRONMENTAL ETCH RESISTANCE OF COATING H AND COATING I USING 0.1 NORMAL PHOSPHORIC ACID	
COATING	TEST RESULTS
H	Contact area was slightly swollen
I	Contact area was swollen

EXAMPLE 8

The procedure of EXAMPLE 3 was repeated using a different acrylic resin, different ratios of CYMEL® 303 crosslinker and 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine co-crosslinker to prepare COATINGS J, K, L, M, and N. The coatings were formulated, applied onto base-coated panels, and cured. The formulations comprise the following:

	COATINGS				
	J	K	L	M	N
TA 39-14 Acrylic Resin (g)	7.80	77.5	72.2	76.5	78.2
CYMEL® 303 Crosslinker	19.8	14.6	11.4	4.7	21.8
2,4,6-tris-(Butoxycarbonylamino)-1,3,5-triazine	2.2	7.9	11.4	18.8	0.0
para-Toluenesulfonic acid	0.4	0.4	0.4	0.4	0.4
Substrate, White Base-Coated Panels ED-11CRS					
Cure Schedule: 125 °C/30 min					

TABLE 10

PHYSICAL AND RESISTANCE PROPERTIES OF COATINGS J, K, L, M AND N						
		COATINGS				
		J	K	L	M	N
Thickness	(mils) (mm)	1.77 0.045	1.65 0.042	1.75 0.044	1.73 0.044	1.75 0.044
Hardness,	KHN ₂₅ Pencil	5.9 F-H	5.8 F-H	5.8 F-H	6.1 F-H	5.9 B-HB
Methyl Ethyl Ketone Rubs, to Mar		200 +	200 +	200 +	200 +	200 +
Adhesion, Top Coat to Base Coat		5	5	5	5	2-3
Closs 20°/60°, Original		86/93	86/93	87/94	86/93	86/93
Yellow Index, Original		-2.4	2.7	-2.1	-2.3	-2.5
After 1st Overbake		-1.8	-2.2	-1.6	-1.7	-1.9
After 2nd Overbake		-1.7	-2.1	-1.4	-1.6	-1.7
Chip Resistance*		5	5-6	5	4-5	5-6

* Chip Resistance scale: 0 is the best, 10 is the worst.

EXAMPLE 9

The procedure of EXAMPLE 8 used to prepare COATING L and COATING N was repeated to prepare COATING O and COATING P, respectively, with the exception that the base coat and the primer were omitted, and the bake temperature was 135°C/30 min.

Coated coupons, enclosed in a glass chamber having humid air blown therethrough at a rate of 50 ml per minute, were heated at 135°C for 30 minutes to cure the coatings. The released formaldehyde was collected and analyzed by a procedure described in an article by J. McClure in Analytical Letters, Volume 21, Number 2, page 253 (1988), the contents of which are incorporated herein by reference. The results are summarized in Table 11.

TABLE 11

FORMALDEHYDE EMISSIONS OF COATING L AND COATING N DURING CURE			
		COATING L	COATING N
THICKNESS,	(mils) (mm)	1.2 0.030	1.2 0.030
HARDNESS, KHN ₂₅		7.2	8.6
FORMALDEHYDE (%)*		1.0	2.0

* Emitted formaldehyde, based on dry film weight.

EXAMPLE 10

The procedure of EXAMPLE 3 was repeated using a formulation comprising a polyester resin instead of an acrylic resin. Further, a portion of the polyester was ground, in a three roll mill with titanium dioxide pigment and thereafter the remaining ingredients were added. COATING Q, COATING R, and COATING S were prepared as before by curing at 125°C for 30 minutes.

The ingredients comprising the formulations and the physical and resistance properties of the cured coatings are summarized in TABLE 12.

TABLE 12

COATING PERFORMANCE OF COATINGS Q, R, AND S IN A PIGMENTED POLYESTER SYSTEM				
		COATING Q	COATING R	COATING S
Grind base:				
Chempol 11-1369 (g)		30.8	30.8	30.8
TiPure R-960 (g)		80.0	80.0	80.0
K-Flex 2302 Polyester Resin (g)		44.4	0.0	0.0
K-Flex 2306 Polyester Resin (g)		0.0	45.7	0.0
Chempol 11-1369 Polyester Resin (g)		0.0	0.0	38.5
2,4,6-tris-(Butoxycarbonylamino)-1,3,5-triazine (g)		24.8	23.5	30.7
Para-Toluenesulfonic Acid (g)		0.4	0.4	0.4
Substrate: Iron Phosphate-treated Cold Roll Steel (CRS)				
Coating performance				
Film thickness,	(mils)	1.2	1.2	1.2
	(mm)	0.030	0.030	0.030
Film hardness,	KHN ₂₅	2.2	4.6	15.8
	pencil	H-2H	H-2H	H-2H
Gloss, 20°/60°		73/89	86/94	82/94
Yellowness index		-3.3	-3.3	-3.8
MEK, rubs,	to mar	120	100	20
	to remove	200 +	200 +	200 +
Direct impact, in-lb		160 +	160 +	120
Reverse impact, in-lb		160 +	160 +	20

Although the present invention has been described with reference to certain preferred embodiments, it is apparent that modifications and changes thereof may be made by those skilled in the art, without departing from the scope of this invention as defined by the appended claims.

Claims

1. A curable composition, comprising:
a polyfunctional hydroxy group containing material;
a triazinetriss-carbamate; and
an acid cure catalyst.
2. The curable composition according to claim 1, further comprising:
an aminoresin crosslinking agent;
3. The curable composition according to claim 1 or 2, wherein the triazin triss-carbamate is a 1,3,5-triazine-2,4,6-tris-carbamate.
4. The curable composition according to one of the preceding claims, wherein the carbamate is selected from the group consisting of:

- (i) 1,3,5-triazine-2,4,6-tris-carbamate of the formula $C_3N_3(NHCOOR)_3$ wherein R in each NHCOOR group is independently selected from the group consisting of an alkyl of 1 to 20 carbon atoms, an aryl of 6 to 20 carbon atoms, an aralkyl of 7 to 20 carbon atoms, and a mixture thereof;
- (ii) an oligomer of (i); and
- 5 (iii) a mixture of (i) and (ii)
5. The curable composition according to one of the preceding claims wherein the polyfunctional hydroxy group containing material is selected from the group consisting of polyols, alkyds, hydroxyfunctional acrylic resins, hydroxyfunctional polyester resins, hydroxyfunctional polyurethane prepolymers, products derived from condensation of epoxy resins with an amine, and a mixture thereof.
- 10 6. The curable composition according to one of claims 2 to 5 wherein the aminoresin crosslinking agent is selected from the group consisting of:
- (I) an alkoxymethyl melamine having two to six alkoxymethyl groups;
- 15 (II) an alkoxymethyl guanamine having two to four alkoxymethyl groups;
- (III) an alkoxymethyl glycoluril having two to four alkoxymethyl groups;
- (IV) an alkoxymethyl urea having two to four alkoxymethyl groups;
- (V) an oligomer of (I), (II), (III), or (IV); and
- (VI) a mixture of at least two of any of (I), (II), (III), (IV), or (V).
- 20 7. The curable composition of claim 6 wherein the aminoresin crosslinking agent comprises N,N',N''-trialkoxymethyl melamine, N,N',N'',N'''-tetraalkoxymethyl glycoluril, oligomers thereof, and a mixture of any of said crosslinking agents.
- 25 8. The curable composition according to one of claims 3 to 7 wherein the carbamate is selected from the group consisting of 2,4,6-tris-(methoxycarbonylamino)-1,3,5-triazine, 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine, and a mixture thereof.
9. The curable composition according to one of the preceding claims wherein the acid cure catalyst is selected from the group consisting of a sulfonic acid, an alkyl or aryl acid phosphate or pyrophosphate, a carboxylic acid, a sulfonimide, a mineral acid, and a mixture thereof.
- 30 10. The curable composition of claim 9 wherein the acid cure catalyst is a sulfonic acid selected from the group consisting of benzenesulfonic acid, para-toluenesulfonic acid, dodecylbenzenesulfonic acid, naphthalene-sulfonic acid, dinonylnaphthalenedisulfonic acid, and a mixture thereof.
- 35 11. The curable composition according to one of claims 2 to 10 wherein the weight ratio of the aminoresin to the carbamate is in the range of from 99:1 to 0.2:1.
- 40 12. The curable composition according to one of claims 2 to 11 wherein the weight ratio of the polyfunctional hydroxy group containing material to the sum of the aminoresin and the carbamate is in the range of from 99:1 to 0.5:1.
13. The curable composition according to one of claims 2 to 12 wherein the weight percent of the acid cure catalyst to the sum of the polyfunctional hydroxy group containing material, the aminoresin, and the carbamate is in the range of from 0.01 weight percent to 3 weight percent.
- 45 14. A curable coating composition, comprising:
- (a) a hydroxyfunctional acrylic or polyester resin;
- 50 (b) an aminoresin crosslinking agent selected from the group consisting of N,N',N''-trialkoxymethyl melamine, N,N',N'',N'',N'''-hexaalkoxymethyl melamine, N,N',N'',N'''-tetraalkoxymethyl glycoluril, oligomers thereof, and a mixture of any of said aminoresin crosslinking agents;
- (c) a carbamate co-crosslinking agent selected from the group consisting of 2,4,6-tris-(methoxycarbonylamino)-1,3,5-triazine, 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine, and a mixture thereof; and
- 55 (d) an acid cure catalyst selected from the group consisting of a sulfonic acid, a dialkyl acid pyrophosphate, and a mixture thereof.
15. The curable coating composition according to claim 14, comprising:

- (a) a hydroxyfunctional acrylic resin;
 (b) an N,N',N''-trimethoxymethyl melamine, an N,N,N',N'',N''-hexamethoxymethyl melamine, oligomers thereof, and mixtures of said melamines;
 (c) 2,4,6-tris-(butoxycarbonylamino)-1,3,5-triazine; and
 5 (d) para-toluenesulfonic acid, dimethyl acid pyrophosphate, or a mixture thereof.
16. The curable coating composition according to claim 15, comprising as component N,N,N',N'',N''-hexamethoxymethyl melamine and as component para-toluenesulfonic acid.
- 10 17. A method of coating a substrate by contacting said substrate with a curable composition comprising:
 (1) a polyfunctional hydroxy group containing material;
 (2) a triazinetriss-carbamate; and
 (3) an acid cure catalyst; and thereafter heat curing said curable composition to produce a
 15 crosslinked film or object.
18. The method according to claim 17, wherein the curable composition further comprises an aminoresin crosslinking agent.
- 20 19. The method according to one of claims 17 or 18, wherein the triazinetriss-carbamate is a 1,3,5-triazine-2,4,6-tris-carbamate.
20. The method according to one of claims 17 to 19, wherein the carbamate is selected from the group consisting of:
 25 (i) 1,3,5-triazine-2,4,6-tris-carbamate of the formula $C_3N_3(NHCOOR)_3$, wherein R in each NHCOOR group is independently selected from the group consisting of an alkyl of 1 to 20 carbon atoms, an aryl of 6 to 20 carbon atoms, an aralkyl of 7 to 20 carbon atoms and a mixture thereof;
 (ii) an oligomer of (i); and
 (iii) a mixture of (i) and (ii).
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21. A film or object obtainable by the method of one of claims 17 to 20.
22. Use of the curable compositions according to one of claims 1 to 16 to form solid articles or to produce adhesives or coatings.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 93 12 0846

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A,D	US-A-4 939 213 (JACOBS, III) * column 10 - column 11; example 9 * * claims 1-4,10,11 * ---	1,3-5,8, 14,17, 21,22	C08K5/3492 C09D161/32
A	EP-A-0 193 517 (MONSANTO COMPANY) * page 13, line 9 - page 14, line 5 * * examples 1-5 * * claims 1,9 * -----	1,2,5-7, 9,10,14, 21,22	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C08K C09D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 April 1994	Examiner Siemens, T
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ----- & : member of the same patent family, corresponding document			